

METEORIC WATER INFILTRATION IN SKALLEN MARBLES, EAST ANTARCTICA: OXYGEN ISOTOPIC EVIDENCE

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Abstract: We report here extremely large millimeter scale oxygen isotopic heterogeneity in calcites from a Skallen marble specimen. The $\delta^{18}\text{O}$ of calcite cores and most of the calcite grain boundaries are grouped around 17‰ while two analyses from the calcite-phlogopite grain boundary show depletion to –1‰. A corresponding $\delta^{13}\text{C}$ enrichment (only 0.7‰) is also observed. The $\delta^{13}\text{C}$ of graphite does not show any heterogeneity. The homogeneity of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ of calcite (except for the local depletion) and $\delta^{13}\text{C}$ of graphite indicate that the marbles evolved through prograde and peak metamorphism with possible internal fluid buffering. The variations observed in carbon and oxygen isotopes can be ascribed to devolatilization reactions. The peak metamorphic temperature estimate by carbon isotope thermometry gave 760°C, consistent with regional peak metamorphic conditions. The local occurrence of isotopic heterogeneity on the calcite-phlogopite boundary suggests that there was meteoric water infiltration during the late stages of metamorphic history. Millimeter scale gigantic oxygen isotopic heterogeneity is observed for the first time in metamorphic rocks. The mechanism of isotope exchange involved is unclear in the present study, but may indicate a process of fluid flow through preferential grain boundaries and by solution-precipitation or diffusion.

key words: Skallen marbles, oxygen isotopes, calcite, meteoric water, fluid infiltration

1. Introduction

Stable isotopes of carbon and oxygen are powerful tools in monitoring fluid-rock interaction processes. Many studies have documented the effect of fluids in modifying isotopic compositions in igneous and metamorphic environments (*e.g.*, VALLEY, 1986). The scale of such studies varies widely from micrometers to tens of kilometers and each has its own significance. While large scale hydrothermal fluid circulation within the crust has been evident in many exposed deep crustal domains and is mainly controlled by the tectonic setting (FERRY, 1992; BUICK *et al.*, 1994; CARTWRIGHT and BUICK, 1995), small scale variations are mostly controlled by the inherent physical and chemical properties of minerals (*e.g.*, EILER *et al.*, 1992). The recent advent of microanalytical techniques has been a revolutionary step in documenting intracrystalline isotopic variations (WADA, 1988; VALLEY and GRAHAM, 1991). Isotopic heterogeneity in metamorphic minerals has been reported in several cases, and may result from either intercrystalline diffusion during cooling from peak metamorphic temperatures (VALLEY and GRAHAM, 1991; EILER *et al.*, 1992) or interaction with grain boundary fluids (*e.g.* ARITA and WADA, 1990). Additionally isotope profiles in zoned minerals can give valuable insight to the time integrated diffusion processes.

Here we report millimeter scale huge oxygen isotopic heterogeneity within a granulite grade marble specimen from Skallen, East Antarctica. The results are used to deduce the source of fluids, timing and extent of diffusion in calcite.

2. Geological Setting of the Studied Sample

The marble sample of the present study is from the Skallen region of the granulite facies Lützow-Holm Complex (Fig. 1A). The Lützow-Holm complex is a granulite to amphibolite facies terrain and the geology in this complex has been studied by several workers (YOSHIDA, 1977, 1978; HIROI *et al.*, 1983, 1986, 1987). Regional peak granulite facies metamorphism at temperatures in the range 760–830°C and pressures of 7 ± 1 kbar has been reported (MOTOYOSHI *et al.*, 1989), with the terrain being exhumed through a clockwise *P-T* trajectory. Recent geochronologic studies indicate that this Proterozoic terrain is tectonothermally affected by the Cambrian orogeny (SHIRAISHI *et al.*, 1994), similar to many parts of East Gondwana (YOSHIDA, 1995). The marble band of the present study crops out in the lower calcareous formation which is interlayered with orthopyroxene bearing charnockites and pelitic aluminous gneisses (Fig. 1B). The sample investigated comprises mineral paragenesis of calcite + forsterite (serpentinised) + phlogopite + spinel + graphite.

3. Analytical Techniques

Stable isotope compositions of carbon and oxygen were determined using a finnigan Mat 250 Mass Spectrometer at Shizuoka University, Japan. The marble sample was cut, polished and stained with alizarin Red S to distinguish between calcite and other carbonates. The calcite samples were then separated using a knife edge by scraping from the polished slab. All the calcites used for analysis in this study were chosen from either the matrix or cores of single calcite crystals. The sketch in Fig. 2 shows the loci of calcite separated from the slab. The pulverized calcite was then placed in a small stainless steel cup and dropped in a reaction vessel containing concentrated phosphoric acid at 60°C in vacuum to liberate CO₂ (WADA *et al.*, 1984a). The reaction vessel was directly connected to the purification line and through to the Mass Spectrometer for isotopic analyses. Machine standards were calibrated to NBS-20 standard. Repeated measurements of the standards yield a $\delta^{13}\text{C}$ reproducibility of 0.03‰ and a $\delta^{18}\text{O}$ of 0.05‰. The results are reported in conventional δ notation relative to the PDB standard for carbon and SMOW standard for oxygen.

Single graphite crystals were obtained by cutting and separating areas having graphite crystals using a microcutter, from the same hand specimen from which calcites were separated for analysis. The graphite was then cleaned with 2N HCl and decanted. The crystals were scooped up by molybdenum mesh, introduced in a Vycor glass tube and the appropriate amount of vanadium pentoxide added. The Vycor glass tubes were preheated at 1100°C for 10 hours, before sample introduction, to remove possible contamination from the tubes (*cf.* WADA *et al.*, 1984b). The graphite samples with vanadium pentoxide were again preheated at 500°C for 30 min to remove any surficial contamination in the sample/reagent. The tubes were then sealed in vacuum and allowed to com-

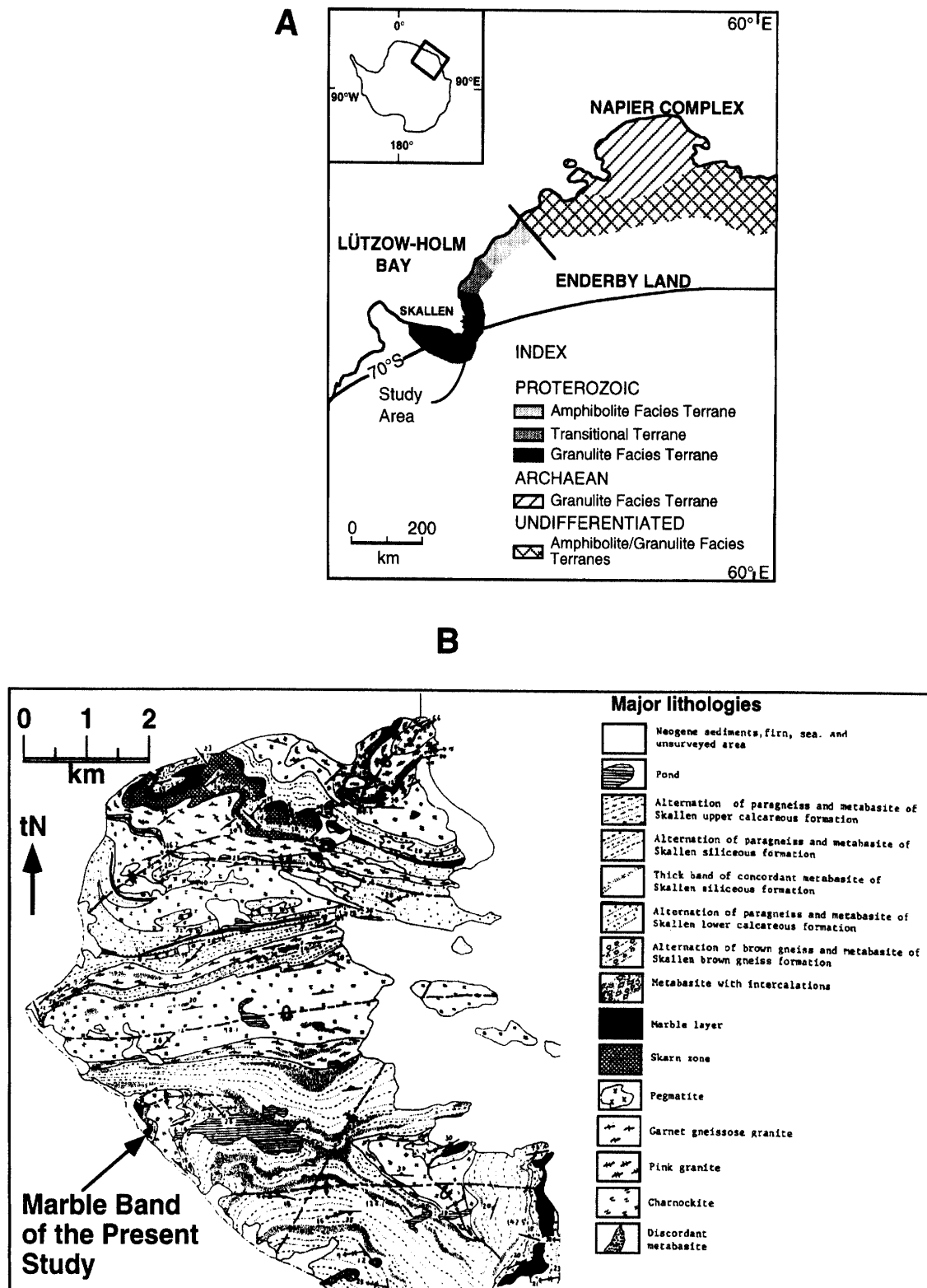


Fig. 1. (A) Generalized geological map of Lützow-Holm complex showing the locality Skallen. Metamorphic zonation of the complex is after HIRAI et al. (1987). (B) Detailed structural and lithologic map of the Skallen area, where the present marble band crops out. Refer to YOSHIDA (1977) for more details about structural evolution and lithologic types.

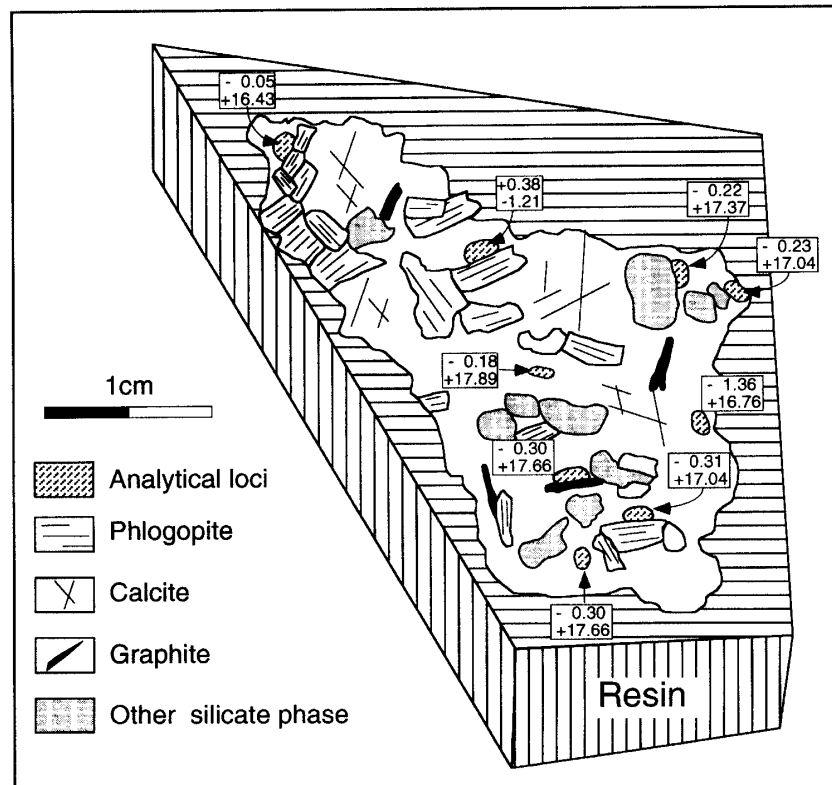


Fig. 2. Sketch of marble specimen showing the analyzed spots. The numerals within square boxes correspond to $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values. Note the extreme depletion of oxygen isotope at the calcite-phlogopite grain boundary.

bust for 2 hours at 1100°C . The released CO_2 was completely used for measuring the isotopes.

4. Results and Discussion

Calcite in association with different minerals and different locii in the same sample were analyzed and the results are presented in the sketch in Fig. 2 and Table 1. The analytical loci include calcite grain core, calcite-calcite grain boundary, calcite-phlogopite grain boundary, calcite-forsterite grain boundary, and calcite-graphite grain boundary. Of the nine analyses from the cut surface (Fig. 2), except for one calcite-phlogopite grain boundary, all the other $\delta^{18}\text{O}$ values are grouped around 17‰ . The calcite-phlogopite grain boundary shows extreme $\delta^{18}\text{O}$ depletion to -1.2‰ . The $\delta^{13}\text{C}$ at this locale also shows a corresponding enrichment ($+0.4\text{‰}$) even though quantitatively the enrichment is very limited. In order to reconfirm the isotopic heterogeneity another cut surface *c.* 1 cm above that shown in Fig. 2 was examined, and two calcite samples from the calcite-phlogopite grain boundary were analyzed. Here also one analysis shows similar extreme $\delta^{18}\text{O}$ depletion (-0.8‰) and $\delta^{13}\text{C}$ enrichment (0.4‰). Two graphite crystals were analyzed for $\delta^{13}\text{C}$ in order to evaluate whether peak metamorphic isotopic homogeneity persists between calcite and graphite in the marble; results are presented in Table 1. Both

Table 1. Carbon and oxygen analytical data of the sample investigated in this study. Also given are the temperature estimations using the calcite-graphite thermometry using different calibrations.

A. Calcite analyses from cut surface in Fig. 2

Sample No	$\delta_{13}\text{C}_{\text{PDB}}$	$\delta_{18}\text{O}_{\text{SMOW}}$	Remarks
cc-5	-0.18	17.89	core of calcite crystal
cc-6	-1.36	16.76	cc-cc grain boundary
cc-7	-0.30	17.66	core of calcite crystal
cc-8	0.38	-1.21	contact with phlogopite
cc-9	-0.22	17.37	contact with forsterite
cc-10	-0.31	17.04	contact with phlogopite
cc-11	-0.15	17.29	contact with graphite
cc-12	-0.23	17.04	core of calcite crystal
cc-13	-0.05	16.43	contact with phlogopite

B. Calcite analyses from cut surface c. 1 cm above the surface in Fig. 2

3cc-1	-0.06	13.96	contact with phlogopite
3cc-2	0.36	-0.86	contact with phlogopite

C. Graphite analyses

Sample No	$\delta_{13}\text{C}_{\text{PDB}}$	Remarks
G-1	-2.49	reflective surfaced single crystal
G-2	-2.66	reflective surfaced single crystal

D. Calcite-graphite temperature estimates

$\Delta(\delta^{13}\text{C}_{\text{cal}} - \delta^{13}\text{C}_{\text{gr}})$	Temperature calibrations (°C)			
	W&S	CCMG	D&V	K&V
2.8	765	915	765	855
2.9	755	870	755	835

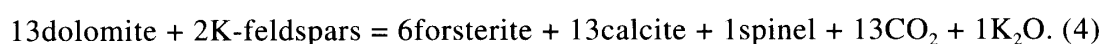
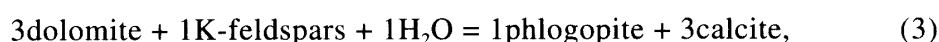
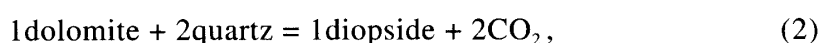
Note: Calcite-graphite temperature calibrations; W&S—WADA and SUZUKI, 1983; CCMG—CHACKO *et al.*, 1991; D&V—DUNN and VALLEY, 1992; K&V—KITCHEN and VALLEY, 1995.

the graphite samples show similar results of about -2.5‰ .

We tried to estimate the peak metamorphic temperature condition in marble using calcite-graphite carbon isotope exchange thermometry. Different calibrations gave different temperature estimates (Table 1). The peak metamorphic temperature in the marble specimen was identified to be around 760°C using the calibrations of DUNN and VALLEY (1992) and WADA and SUZUKI (1983). These temperature estimates of peak metamorphism in the marbles are consistent with the regional peak metamorphic temperature estimates (MOTOYOSHI *et al.*, 1989; SANTOSH and YOSHIDA, 1992). The perfect crystalline nature of graphite as well as the absence of carbon isotope variations in calcite can account for the isotopic equilibrium between calcite and graphite in these marbles, indicating the reliability of applying carbon isotope thermometry in Skallen marbles.

Skallen marbles are thought to have been initially deposited as impure carbonaceous

sediments during the Proterozoic period. Comparing with the carbon and oxygen isotope ratios of the carbonate lithologies of this period ($22 \pm 5\text{‰}$ and $2 \pm 2\text{‰}$ for $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ respectively, *cf.* VEIZER and HOEFS, 1976), the $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ values of Skallen marbles fall within the same range. The $\delta^{18}\text{O}$ of Skallen marbles lies in the depleted part of the range of Proterozoic isotopic values. During prograde metamorphism of siliceous limestones, decarbonation reactions (FERRY, 1991) tend to lower the initially high $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ ratios of originally sedimentary carbonates. The prograde decarbonation and dehydration reactions produce considerable amounts of fluids which act as carriers of isotopes between phases. The isotope exchange is considerably controlled by the carbonate-silicate mineral ratio in the original rock. The pronounced presence of calc-silicate minerals like forsterite and phlogopite attest to this possibility, and the following decarbonation reactions might have proceeded during the prograde metamorphism of Skallen marbles resulting in the depletion of $\delta^{18}\text{O}$.



The above reactions progress with the liberation of CO_2 and may consume water if the product phase can stoichiometrically accommodate it.

Apparently during the prograde or peak metamorphism there was possibly no fluid infiltration, the $\delta^{18}\text{O}$ of the marbles can be considered to have evolved through prograde devolatilizing reactions. Similarly, the carbon isotopes fractionated between calcite and graphite during metamorphism, resulting in the resetting and equilibration of carbon

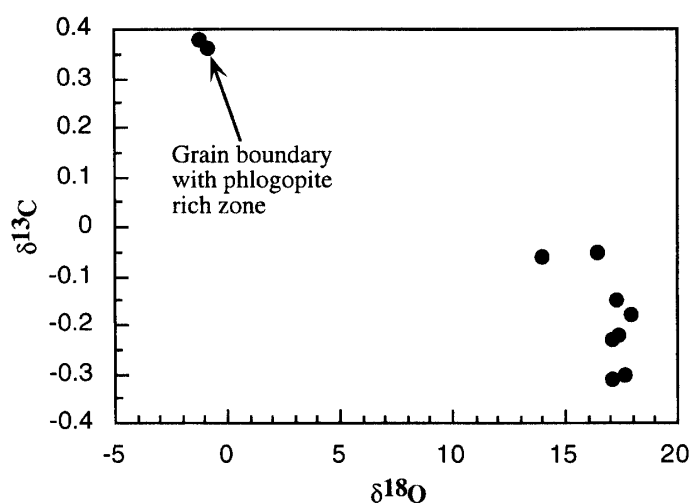


Fig. 3. $\delta^{18}\text{O}$ versus $\delta^{13}\text{C}$ relation with a coupled isotopic variation observed where heterogeneity occurs.

isotopic ratios.

The extreme depletion of $\delta^{18}\text{O}$ in calcite grain boundaries can only be explained by open system fluid infiltration. The absence of complete homogenization of marbles indicates that the fluid infiltration occurred during late stages of metamorphic history and through preferential grain boundaries. TSUCHIYA *et al.* (1992), reporting carbon and oxygen isotopic profiles within marbles from the Sør Rondane Mountains, East Antarctica, modeled the coupled depletion toward lithologic boundaries resulting from metamorphic fluid flow by diffusion and advection.

Late stage fluid infiltration in granulites has been reported from the Adirondack Highlands, where hydrothermal fluids infiltrated the terrain at 300–500°C (MORRISON and VALLEY, 1989, 1991). The extreme oxygen isotopic depletion in the present study can be correlated with late stage hydrothermal fluid infiltration into the marbles; the infiltration was locally controlled, probably by differing physical properties of grain boundaries. Equilibrium dihedral angles is one among the important properties, controlling the fluid flow through grain boundaries. Studies on marble assemblages have shown that calcite-calcite grain boundaries are difficult pathways for fluids (HOLNESS and GRAHAM, 1991), and we presume that this might have restricted the fluid infiltration in Skallen marbles to either calcite-phlogopite grain boundaries or hydrofractures. The present data point to a heterogeneous distribution of oxygen isotope depletion when viewed two dimensionally, but if considered in three dimensions oxygen isotope depletion occurs in a zone which is rich in phlogopite. This suggests that the phlogopite-calcite boundary in this zone acted as a channel for infiltrating fluids.

Alternatively, the zone represents a weak plane where differential stress developed fractures, due to the anisotropic physical properties of different minerals (KRANTZ, 1983), through which fluids infiltrated. The presence of fluids enhances the development of microfractures in rocks when the local stress exceeds the local strength (WORDEN *et al.*, 1990). If fracturing is accompanied by fluid infiltration and isotope exchange by solution-precipitation and/or diffusion, then it is possible to find such isotopic heterogeneity in rocks.

The possible mechanisms of isotope exchange in minerals during hydrothermal alteration are grain boundary diffusion, solution-precipitation and exchange along microfractures (ELSENHEIMER and VALLEY, 1993). Petrographic studies on the marble sample in the present study did not reveal any healed fractures within calcite crystals and the isotopic heterogeneity observed is confined to the calcite-phlogopite grain boundary only. This suggests that exchange along microfractures within the calcite crystals may not be the cause of such a heterogeneity. Diffusion of isotopes between two phase will result in a sigmoidal profile across the grain boundary, but here we can find an abrupt isotopic heterogeneity within the limit of the scale we have examined. Further detailed microscale studies will possibly give a clearer picture about the process involved during the isotopic exchange.

Since factors such as the oxygen self diffusion in water at high pressures and temperatures, and the temperature of fluid infiltration, are unknown, the original $\delta^{18}\text{O}$ composition of the hydrothermal fluids is difficult to determine. But it can be assumed that the infiltrating fluids have the $\delta^{18}\text{O}$ values less than or equal to -1‰ . Thus it can be assumed that the source for these fluids is definitely meteoric (SHEPPARD, 1986). The

composition of fluids cannot be exactly determined, since there exists a coupled variation of $\delta^{18}\text{O}$ and $\delta^{13}\text{C}$ in these calcite-phlogopite boundary where isotopic heterogeneity exists (Fig. 3). Clearly the fluids which have infiltrated are not pure aqueous fluids and have carbonic components.

The present results, thus, provide the first direct evidence for late stage millimeter scale hydrothermal meteoric fluid infiltration in granulites.

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References

- ARITA, Y. and WADA, H. (1990): Stable isotope evidence for migration of metamorphic fluids along grain boundaries of marbles. *Geochim. J.*, **24**, 173–186.
- BUICK, I.S., CARTWRIGHT, I., HAND, M. and POWELL, R. (1994): Evidence of pre-regional metamorphic fluid infiltration of the lower Calcsilicate Unit, Reynolds Range Group (central Australia). *J. Metamorphic Geol.*, **12**, 789–810.
- CARTWRIGHT, I. and BUICK, I.S. (1995): Formation of wollastonite-bearing marbles during late regional metamorphic channelled fluid flow in the Upper Calcsilicate Unit of the Reynolds Range Group, Central Australia. *J. Metamorphic Geol.*, **13**, 397–417.
- CHACKO, T., MAYEDA, T.K., CLAYTON, R.N. and GOLDSMITH, J.R. (1991): Oxygen and carbon isotope fractionations between CO_2 and calcite. *Geochim. Cosmochim. Acta*, **55**, 2867–2882.
- DUNN, S.R. and VALLEY, J.W. (1992): Calcite-graphite isotope thermometry: A test for polymetamorphism in marble, Tudor gabbro aureole, Ontario, Canada. *J. Metamorphic Geol.*, **10**, 487–501.
- EILER, J.M., BAUMGARTNER, L.P. and VALLEY, J.W. (1992): Intercrystalline stable isotope diffusion: A fast grain boundary model. *Contrib. Mineral. Petrol.*, **112**, 543–557.
- ELSENHEIMER, D. and VALLEY, J.W. (1993): Submillimeter scale zonation of $\delta^{18}\text{O}$ in quartz and feldspar, Isle of Skye, Scotland. *Geochim. Cosmochim. Acta*, **57**, 3669–3676.
- FERRY, J.M. (1991): Dehydration and decarbonation reactions as a record of fluid infiltration. *Mineral. Soc. Am. Rev. Mineral.*, **26**, 351–393.
- FERRY, J.M. (1992): Regional metamorphism of the Waits River Formation, eastern Vermont: Delineation of a new type of giant metamorphic hydrothermal system. *J. Petrol.*, **33**, 45–94.
- HIROI, Y., SHIRAISHI, K., YANAI, K. and KIZAKI, K. (1983): Aluminum silicates in the Prince Olav and Sôya Coasts, East Antarctica. *Mem. Natl Inst Polar Res., Spec. Issue*, **28**, 115–131.
- HIROI, Y., SHIRAISHI, K., MOTOYOSHI, Y., KANISAWA, S., YANAI, K. and KIZAKI, K. (1986): Mode of occurrence, bulk chemical compositions, and mineral textures of ultramafic rocks in the Lützow-Holm complex, East Antarctica. *Mem. Natl Inst. Polar Res., Spec. Issue*, **43**, 62–84.
- HIROI, Y., SHIRAISHI, K., MOTOYOSHI, Y. and KATSUSHIMA, T. (1987): Progressive metamorphism of calc-silicate rocks from the Prince Olav and Sôya Coasts, East Antarctica. *Proc. NIPR Symp. Antarct. Geosci.*, **1**, 73–97.
- HOLNESS, M.B. and GRAHAM, C.M. (1991): Equilibrium dihedral angles in the system $\text{H}_2\text{O}-\text{CO}_2-\text{NaCl}$ -calcite, and implications for fluid flow during metamorphism. *Contrib. Mineral. Petrol.*, **108**, 368–383.
- KITCHEN, N. E. and VALLEY, J.W. (1995): Carbon isotope thermometry in marbles of the Adirondack Mountains, New York. *J. Metamorphic Geol.*, **13**, 577–594.

- KRANTZ, R.L. (1983) Micro-cracks in rocks: a review. *Tectonophysics*, **100**, 449–480.
- MORRISON, J. and VALLEY, J.W. (1989): Post-granulite facies fluid infiltration in the Adirondack Mountains. *Geology*, **16**, 513–516.
- MORRISON, J. and VALLEY, J.W. (1991): Contamination of the Marcy Anorthosite massif, Adirondack Mountains, N.Y.: Petrologic and isotopic evidence. *Contrib. Mineral. Petrol.*, **98**, 97–108.
- MOTOYOSHI, Y., MATSUBARA, S. and MATSUEDA, H. (1989): P-T evolution of the granulite-facies rocks of the Lützow Holm Bay region, East Antarctica. *Evolution of Metamorphic Belts*, ed. by J.S. DALY *et al.* Oxford, Blackwell, 325–329 (Geol. Soc. Spec. Publ., No. 43).
- SANTOSH, M. and YOSHIDA, M. (1992): A petrologic and fluid inclusion study of charnockites from the Lützow-Holm Bay region, East Antarctica: Evidence for fluid-rich metamorphism in the lower crust. *Lithos*, **29**, 107–126.
- SHEPPARD, S.M.F. (1986): Characterisation and isotopic variations in natural waters. *Mineral. Soc. Am. Rev. Mineral.*, **16**, 165–184.
- SHIRAISHI, K., ELLIS, D.J., HIROI, Y., FANNING, C.M., MOTOYOSHI, Y. and NAKAI, Y. (1994): Cambrian orogenic belt in East Antarctica and Sri Lanka: Implications for Gondwana assembly. *J. Geol.*, **102**, 47–65.
- TSUCHIYA, N., OSANAI, Y. and WADA, H. (1992): Carbon and oxygen isotopic compositions of marbles from the Sør Rondane Mountains, East Antarctica. *Recent Progress in Antarctic Earth Science*, ed. by Y. YOSHIDA *et al.* Tokyo, Terra Sci. Publ., 55–59.
- VALLEY, J.W. (1986): Stable isotope geochemistry of metamorphic rocks. *Mineral. Soc. Am. Rev. Mineral.*, **16**, 445–490.
- VALLEY, J.W. and GRAHAM, C.M. (1991): Ion microprobe analysis of oxygen isotope ratios in granulite facies magnetites: diffusive exchange as a guide to cooling history. *Contrib. Mineral. Petrol.*, **109**, 38–52.
- VEIZER, J. and HOEFS, J. (1976): The nature of $^{18}\text{O}/^{16}\text{O}$ and $^{13}\text{C}/^{12}\text{C}$ secular trends in sedimentary carbonate rocks. *Geochim. Cosmochim. Acta*, **40**, 1387–1395.
- WADA, H. (1988): Microscale isotopic zoning in calcite and graphite crystals in marble. *Nature*, **331**, 61–63.
- WADA, H. and SUZUKI, K. (1983): Carbon isotope thermometry calibrated by dolomite-calcite solvus temperatures. *Geochim. Cosmochim. Acta*, **47**, 697–706.
- WADA, H., FUJII, N. and NIITSUMA, N. (1984a): Analytical method of stable isotope for ultra-small amounts of carbon dioxide with MAT-250 mass spectrometer. *Geosci. Rep. Shizuoka Univ.*, **10**, 103–112 (in Japanese with English abstract).
- WADA, H., ITO, R. and AKIYAMA, F. (1984b): Preparation and measurement of carbon dioxide for stable isotope analysis of small amount of graphite. *Geosci. Rep. Shizuoka Univ.*, **10**, 133–141 (in Japanese with English abstract).
- WORDEN, R.H., WALKER, F.D.L., PARSONS, I. and BROWN, W.L. (1990) Development of microporosity, diffusion channels and dueteric coarsening in perthitic alkali feldspars. *Contrib. Mineral. Petrol.*, **104**, 307–515.
- YOSHIDA, M. (1977): Geology of the Skallen region, Lützow-Holmbukta, East Antarctica. *Mem. Natl Inst. Polar Res., Ser. C (Earth Sci.)*, **11**, 38p.
- YOSHIDA, M. (1978): Tectonics and petrology of charnockites around Lützow-Holmbukta, East Antarctica. *J. Geosci., Osaka City Univ.*, **21**, 65–152.
- YOSHIDA, M. (1995): Assembly of East Gondwanaland during the Mesoproterozoic and its rejuvenation during the Pan-African period. *Geol. Soc. India, Mem.*, **34**, 25–45.

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